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Catalysis of gold and gold-silver alloy nanoparticles supported on mesoporous silica

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Abstract: We used surface amino-functionalized mesoporous silica to confine gold or gold/silver alloy nanoparticles inside the nanochannel with uniform size distribution of particle sizes. Many characterization techniques were used to study the catalyst system, such as nitrogen adsorption, TEM, XRD, EXAFS (X-ray absorption fine structure spectroscopy), and UV-vis spectroscopy. Herein, supported Au-Ag alloy nanoparticles have been proved to exhibit superior activity for CO oxidation at low temperature, not only in the absence of hydrogen, but under H₂-rich atmosphere.

Introduction:

Proton exchange membrane fuel cells (PEMFC) have been extensively studied in the past decade¹. Pure hydrogen source is the ideal fuel for mobile energy systems. However, the Pt anode catalysts would be significantly poisoned by traces of CO in reformed gases. To fulfill the high purification requirement, the preferential oxidation of CO (PROX) appears as the most promising approach and the lowest cost technique. In general, the premise for good PROX performance is to choose a catalyst with more oxidation activity for CO than for H₂. Recently we found that both Au and Au-Ag alloy catalyst showed a high activity and selectivity. Mesoporous aluminosilicates MCM-41 was chosen as the support while previous study often used the basic metal oxide as support in PROX reaction¹. Behm *et al* showed that basic supports easily form surface carbonates under selective CO oxidation². Carbonates would then affect the activity and stability of the catalysts greatly and an acidic silica support may solve this problem. Our purpose here is to develop stable gold-based nanocatalysts for the removal of CO in the hydrogen produced from reformed gas. The hydrogen gas then can be used in fuel cell applications.

Mesoporous aluminosilicate materials seem to be an ideal host for supporting metallic nanoparticles due to well-defined pores and ability of surface functionalization. A channel system of pore sizes in the range of 3 to 5 nm, the optimum size for catalysis, with rigid pore walls would limit the size of confined gold. In this work, we have successfully employed propylamine-functionalized Al-SBA-15 and MCM-41 silica to confine Au and Au/Ag nanoparticles for catalysis study.

Experiment:

In this work, we demonstrated surface functionalized mesoporous silica as supporting host to confine the alloy nanoparticles. The silica surface was modified by APTS (H₂N(CH₂)₃-Si(OMe)₃) in a direct method of adsorption of gold/silver precursor and then reduction³. The confinement of nanochannel would produce uniform sized metal nanoparticles. Various characterization techniques were used to study the catalyst system, such as nitrogen adsorption, TEM, XRD, EXAFS (X-ray absorption fine structure spectroscopy), and UV-vis spectroscopy. Especially, EXAFS was employed to determine the coordination number and the degree of alloying formation.⁴

Activity test for CO oxidation was carried out with 20mg of catalyst, which were treated with hydrogen at 600°C prior to reaction. The reactant gases contained 1% CO, 1% O₂ for H₂-free atmosphere, and another 60% of H₂ for PROX reaction. The total flow rate was modulated with helium to 33 mL min⁻¹ (GHSV = 100,000 g_{cat}⁻¹ h⁻¹) under atmospheric pressure. The effluent gas was detected by an online gas chromatograph (HP6820) equipped with a Carboxen1000 column and a thermal conductivity detector

(TCD)

Results and Discussion:

(1) Au system: We first demonstrate the use of pure gold nanocatalyst in catalysis of CO oxidation. While there are a large number of recent studies of Au nanocatalysts supported on metal oxides, low-temperature CO oxidation under an acidic environment has not yet been accomplished. Over a novel acidic Al-SBA-15 support, uniformly distributed gold nanoparticles with sizes ~ 2.7 nm were obtained by a successive procedure of aminosilane grafting, gold adsorption-reduction, and then high-temperature hydrogen treatment. The catalyst system, Au@Al-SBA-15, exhibits a high activity for CO oxidation at 80 °C. By varying the Si/Al ratio of the support, the dependence of the catalytic activity on the support Si/Al ratio was found in the CO oxidation reaction.

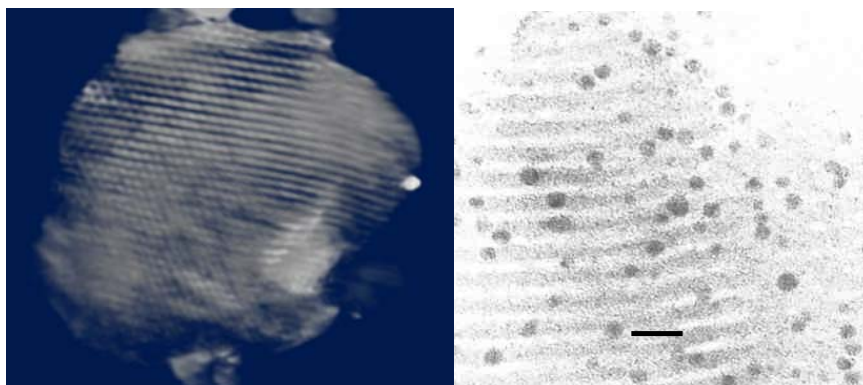


Figure 1. Left: TEM image of the mesoporous silica Al-SBA-15. Right: TEM image of the gold nanoparticles supported in the nanochannels of Al-SBA-15. Scale bar is 20 nm.

This shows that indeed the method of making of supported Au nanoparticles can control the size very well in the range of ~ 3 nm which is optimum for catalytic activity. We then move on to try to make Au/Ag alloy nanoparticles of uniform size in the next section..

(2) Au/Ag system:

Having proved that our mesoporous silica materials will be a good host for uniform metal nanoparticles, we then try alloy metal system. A way for improving on gold nanocatalyst to obtain an active catalyst for CO oxidation is to make gold alloy nanoparticles with a metal of stronger reduction tendency. In this case, the electron transfer to oxygen would be stronger, while one can still have good CO adsorption. Previously, we have found Au and Ag alloy nanoparticles are excellent nanocatalyst for CO oxidation. However, the oxidation was done without the presence of hydrogen. PROX in hydrogen rich environment is a much harder problem. We now investigate the AuAg alloy nanoparticles for PROX.

We determined textural properties of the calcined catalysts with different Au/Ag molar ratios by nitrogen absorption-desorption isotherm obtained at 77K. The BET surface areas of the catalysts were between 650 and 700 m²/g and the pore sizes were all at 2.3 nm. The metal loading amount and gold to silver ratio were determined by ICP-AES and the total loading amount was controlled around 5 wt %. We used XRD and TEM to measure the alloy metal sizes. Both of them showed alloy sizes were about 5nm and the results proved the surface modification method can effectively control the alloy size. In PROX reaction, alloy catalysts showed much better activity toward CO conversion than both pure gold and pure silver catalysts. Alloy catalysts owned near 100% CO conversion at 80°C (see Figure 2) but pure gold catalyst only owned 60% conversion at the same temperature. Moreover, in PROX reaction, alloy catalysts can maintain about 70% of selectivity at 40-80°C. The optimum performance of catalysis is at 80 °C which is the desirable operation temperature for low temperature fuel cells.

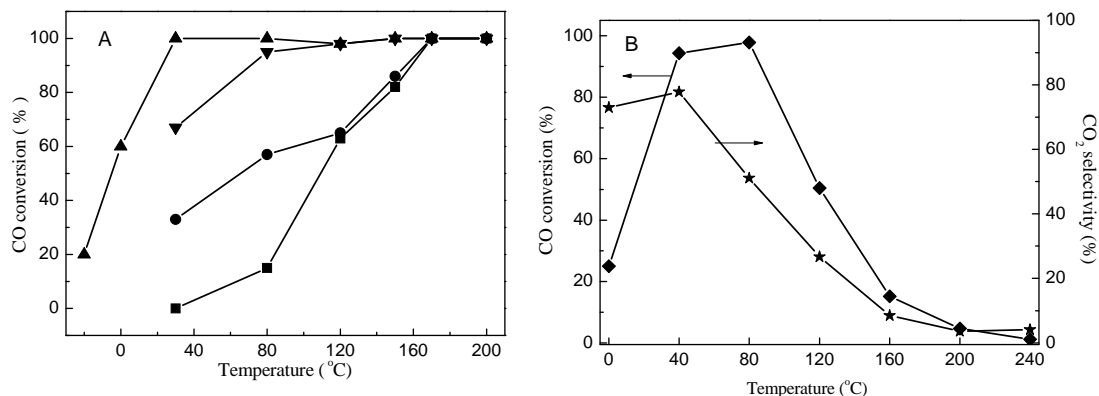


Figure 2. (A) CO conversion profiles versus reaction temperature under H₂-free atmosphere over 4 catalysts with Au/Ag molar ratios of: (■) 0/1, (●) 1/0, (▼) 4/1, and (▲) 8/1. (B) CO conversion (♦) and CO₂ selectivity (★) in PROX reaction over Au/Ag=5/1 catalyst.

We have shown the gold and silver alloy particles could be confined in nano-scale with surface modified mesoporous aluminosilicate MCM-41. Compared with monometallic Au or Ag catalysts, the alloy catalysts show a high performance for CO oxidation at low temperature, and good CO₂ selectivity in the present of hydrogen. In this alloy system, Ag played a key role for oxygen activation, and showing a strongly synergistic effect between Au and Ag.

List of Publications:

Chun-Wan Yen, Meng-Liang Lin, Aiqin Wang, and Chung-Yuan Mou, 2009 "CO oxidation catalyzed by Au-Ag alloy nanoparticle confined in mesoporous silica" *J. Phys Chem C*, 113, 17831-1783